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13. ABSTRACT *(Maximum 200 words)*

The major aim of our research has been a theoretical investigation of (1)
important point defect complexes in low-temperature-grown (LT) GaAs and (2)
the microscopic processes occuring at the surface during growth of GaAs films,
which determine how much excess arsenic will be incorporated into the material.

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Final Technical Report

Theoretical Investigation of Point Defects and Defect Complexes in Low-Temperature-Grown GaAs

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Table of Contents

1. Introduction

The major aim of our research has been a theoretical investigation of
(1) important point defects and defect complexes in low-temperature-grown (LT) GaAs and
(2) the microscopic processes occurring at the surface during growth of GaAs films, which
determine how much excess arsenic will be incorporated into the material.

We have used first-principles pseudopotential calculations to identify and study the low energy defect configurations which can accommodate the excess arsenic that is present in LT GaAs, and to study the technologically important dopant beryllium. We have studied the interactions between these defects, and the mechanisms and energetics of defect motion and transformation (including diffusion, transitions into and out of metastable states, and complex formation and breakup). We have studied the structure of these defects near the cleavage surface of GaAs, and generated simulated STM images of defects containing excess arsenic at the cleavage surface for comparison with experiment, using the Tersoff-Hamann method.[1]

We have also used first-principles calculations to study the dynamics and energetics of the microscopic processes occurring at the growing GaAs surface - particularly the adsorption, diffusion, and incorporation of arsenic at the surface. We have identified the initial steps which occur during nucleation of a new layer, and determined how stoichiometry is controlled during growth, and under which conditions this control will break down. The knowledge we have gained from these first-principles calculations has been used to develop some preliminary Monte Carlo programs to simulate growth on experimentally relevant time scales.[2-3]

In order to accomplish this work, we performed density-functional calculations using both the local density approximation (LDA) and the generalized gradient approximation (GGA),[4] to maximize accuracy and facilitate comparison with earlier calculations. With the exception of a couple of early papers cited in section 2.1, which used calculations based on the Sankey-Niklewski method,[5] which is implemented in terms of a basis of pseudoatomic orbitals, all of the work reported here was based on fully self-consistent calculations using a plane wave basis and the codes developed at the Fritz-Haber-Institut der Max-Planck-Gesellschaft.[6] These calculations used fully separable, norm-conserving pseudopotentials[7-9] constructed from an all-electron

atomic calculation to describe the electron-ion interaction. Gonze's analysis[10] was used to confirm that unphysical ghost states were not present in the separable representation. The Principal Investigator has coauthored a manual[11] covering a later generation of this density-functional code, including some innovations which she helped to develop and test while on sabbatical at the Fritz-Haber-Institut der Max-Planck-Gesellschaft in 1997-98. This manual was used for the international course on "Calculation of Material Properties using Total Energy and Force Methods and *ab initio* Molecular Dynamics", in Trieste, Italy, in August 1999, and is available at http://www.fhi-berlin.mpg.de/th/fhi98md/.

2. Properties of excess-arsenic-containing point defects and defect complexes

2.1 Arsenic interstitials and interstitial-containing complexes

Interstitials are the most complicated of the simple point defects, and the most elusive. For example, even though arsenic interstitials must be created by irradiation of GaAs with sufficiently energetic particles, and they can subsequently be observed to recombine with arsenic vacancies when the sample is heated above 220 °C, isolated arsenic interstitials have not been observed directly in EPR, electrical, or optical experiments.[12] X-ray diffuse scattering[13] and quasi-forbidden X-ray reflection intensity measurements[14] on GaAs grown by the horizontal Bridgman and liquid-encapsulated Czochralski methods provide evidence for the presence of substantial concentrations of defects which are believed to be arsenic interstitials. However, the microscopic structure of these defects cannot be unambiguously determined from these experiments. An extensive analysis[15] of titration experiments and measurements of the density and lattice parameter of melt-grown GaAs has also been cited as evidence that arsenic interstitials are the most numerous defect in melt-grown GaAs at growth.

We have investigated the properties of arsenic interstitials and arsenic interstitial pairs[16] with plane-wave, density-functional calculations using the fhi98md[6] code. This first-principles method is accurate enough to allow us to calculate the formation energy of arsenic-containing defects in the arsenic-rich limit, *i. e.* relative to an arsenic reservoir with the same chemical potential as bulk arsenic. We find that arsenic antisites will be more numerous than arsenic interstitials and interstitial pairs in equilibrium, in the arsenic-rich limit. However, the relative stability of the nearest-neighbor pair of interstitials over two isolated arsenic interstitials[16-17] provides a possible mechanism for the formation of the observed "diffuse clouds" of arsenic interstitials[13-14] in quenched, melt-grown GaAs, if quenching from the melt produces high, non-equilibrium concentrations of interstitials.

Since arsenic interstitials are expected to be quite mobile, if they exist as more than transient defects in GaAs, they are likely to be present predominantly in interstitial-containing complexes, rather than as isolated interstitials. In low-temperature-grown GaAs, which can have up to 1-2% excess arsenic, there are high concentrations of arsenic antisites. This suggests that

low-energy complexes of arsenic interstitials with arsenic antisites may be present in this material.

We have found two low-energy complexes containing an arsenic interstitial and an arsenic antisite. We have called the lowest energy antisite-interstitial complex a "split antisite",[18] since it consists of two arsenic atoms sharing a gallium site, each displaced from the site roughly in the positive or negative (120) direction. This configuration is similar to the lowest energy arsenic interstitial configuration in LT GaAs, which is a "split interstitial" configuration consisting of two arsenic atoms sharing an arsenic site, each displaced from the site roughly in the positive or negative (110) direction.[19,18] The split antisite complex will not be seen as an antisite in EPR or absorption experiments.[18]

The other low-energy complex of an arsenic antisite and an arsenic interstitial which we have found contains a minimally distorted arsenic antisite, with a split interstitial as one of its nearest neighbors.[18, 20-21] The electronic band structure of this complex contains an arsenic antisite-derived level in the midgap region and an antisite-derived resonance in the conduction band. Therefore, this complex will have the EPR and absorption signature characteristic of an arsenic antisite. The binding energies of the split antisite and the nearest-neighbor antisite-interstitial complex are low, suggesting that these complexes may be continually forming, breaking up, and transforming into each other.[18] Therefore, these interstitial-antisite complexes may be responsible for a donor band, instead of two separate donor levels. Our results suggest[18] that the properties of these antisite-interstitial complexes match the properties of the defects responsible for the donor band which lies between 0.3 and 0.5 eV below the conduction band, which is quite prominent in some GaAs samples grown around 350° C at the University of California at Santa Barbara.[22] Like the defects responsible for this band, the nearest-neighbor complex has the EPR and absorption signatures characteristic of an arsenic antisite. Like the defects responsible for this band, and unlike the isolated antisite, antisite-interstitial complexes are unphotoquenchable.

In order to help identify antisite-interstitial complexes in experimental STM pictures of LT GaAs samples, we have rerelaxed these complexes in many different orientations and at different depths below the (110) cleavage surface, in order to find out which configurations are

both stable near the surface and energetically favorable. Based on our results, we believe that if an arsenic antisite is in the third layer down from the surface, an arsenic interstitial bound to that antisite may oscillate rapidly between sharing that site as a split antisite, and occupying each of the four nearest-neighbor sites to the antisite. When the interstitial is occupying the neighboring split interstitial site in the second layer, and is oriented parallel to the surface, we found that it should be visible in STM pictures of the surface, since the electronic charge density associated with the localized interstitial state in the lower part of the gap sticks out strongly perpendicular to the surface.

The simulated STM image we obtained for the split interstitial bound to an antisite in a lower layer looks very similar to the STM picture we obtained for an isolated arsenic interstitial in the same orientation in the second layer. However, an isolated interstitial may not remain just below the surface long enough to be observed, but an interstitial which is bound to an antisite may remain just below the surface longer. Since an interstitial which is bound to an antisite in the third layer is not visible in STM pictures of the surface when it moves down to become a split antisite or occupy one of the lower nearest-neighbor sites of the antisite to which it is bound, if it oscillates rapidly into and out of the second-layer site in which it is visible, the time-averaged STM picture of the interstitial will be weakened by about a factor of 1/5, reflecting the amount of time that the interstitial spends in the site where it is visible. We have provided a simulated STM picture of this complex to Petra Specht and Nikos Jaeger of Eicke Weber's group at the University of California at Berkeley, for comparison to their experimental STM images of the cleaved LT GaAs surface.

Since a major part of the work summarized in this section was carried out by students supported on the affiliated AFOSR grant F49620-97-1-0479, "Augmented Student Participation in Theoretical Investigation of Point Defects and Defect Complexes in Low-Temperature-Grown GaAs", this work will be described in greater detail and figures showing the results will be included in the final report for this grant, which concludes in June, 2001, as well as in our papers cited in this section and other papers which are in preparation.

2.2 Interactions of excess arsenic with Be in Be-doped LT GaAs

Addition of dopants such as Be to arsenide-based semiconductors can reduce arsenic diffusion and arsenic precipitate formation,[23] tune lattice mismatch,[24] and stabilize desirable defects.[24] Therefore it is important to understand how these dopants affect arsenic diffusion and interact with native defects containing excess arsenic.

In order to understand the more rapid than expected strain compensation which is produced by adding Be to LT GaAs, we have investigated the lattice strain induced by the different charge states of arsenic antisites and substitutional beryllium in Be-doped LT GaAs. We find that the lattice strain induced by a substitutional beryllium atom is relatively independent of its charge state - the calculated average distance from a substitutional beryllium atom to its nearest neighbors is smaller than the ideal bond length in GaAs by about 6% for both Be_{Ga}^0 and Be_{Ga}^{-1}. However, we find that the lattice strain induced by an arsenic antisite is strongly dependent on its charge state - the calculated average distance from an arsenic antisite to its nearest neighbors is larger than the ideal Ga-As bond length in GaAs by about 6%, 4%, and 2% for As_{Ga}^0, As_{Ga}^{+1}, and As_{Ga}^{+2}, respectively. This significant decrease in the lattice strain contributed by charged antisites can explain the unexpectedly rapid disappearance of the lattice strain when Be is added to LT GaAs, since the addition of Be increases the fraction of arsenic antisites which are charged.

The calculated bond lengths for the arsenic antisites do not agree with the antisite bond lengths deduced from the experimentally measured change in lattice constant by using Vegard's Law, and assuming that the measured change in lattice constant in undoped LT GaAs is due entirely to arsenic antisites. This experimental analysis[25] indicates that the nearest neighbor distance is expanded by about 12% for arsenic antisites, and decreased by about 6% for beryllium. The discrepancy between the calculated value and the value deduced from experiment for arsenic antisites may be due to neglecting contributions to the lattice strain in undoped LT GaAs from other point defects and extended defects.

2.3 Diffusion in Be-doped and undoped LT GaAs

Since it has been suggested that formation of antisite-beryllium complexes may suppress arsenic antisite diffusion, and therefore cause the unexpectedly slow growth of As precipitates during annealing which has been observed when Be is added to LT GaAs,[23] we have calculated the formation energies of arsenic antisite-beryllium complexes. We found a formation energy of about 0.77 eV for the complex consisting of a single substitutional beryllium and an arsenic antisite, relative to an isolated, neutral antisite and an isolated, neutral substitutional beryllium. However, practically all of this formation energy is due to the exchange of an electron from the donor antisite to the beryllium acceptor - the formation energy of the complex relative to an isolated As_{Ga}^{+1} and an isolated Be_{Ga}^{-1} is considerably less than 0.1 eV. Therefore, although the addition of a large number of substitutional beryllium acceptors allows a comparable number of arsenic antisites to become charged, we expect that these charged defects will not form complexes in appreciable numbers.

The low formation energy for arsenic antisite-substitutional beryllium complexes is actually not very surprising, since both of these defects reside on gallium sites, so they cannot approach closer than a second-neighbor distance in the complex. For this reason, we expect that the situation in LT Be-doped InGaAs will be similar: formation of arsenic antisite-substitutional beryllium complexes is unlikely to play a significant role.

Since our calculations indicate that complexes of substitutional beryllium with arsenic antisites should not play an important role in Be-doped LT GaAs, and the experimental evidence indicates that there are not large numbers of Be interstitials in this material, we cannot use interactions between individual point defects to explain the observed suppression of As precipitate growth in Be-doped LT GaAs. Other possible explanations for the suppression of As precipitate growth could include any increase in the number or changes in the kind of extended defects which might occur when Be is added to LT GaAs, since extended defects may trap the As antisites. Strong local strains may also play a role in trapping the antisites, if there is significant clustering of either the Be or the antisites. We note that such clustering is possible, since during growth it is easier for As antisites to be incorporated in the area above another antisite, where the bonds are already stretched, and for Be to be incorporated in the area above another substitutional

Be atom, where the bonds are already compressed. A third possibility, which has already been suggested by Martina Luysberg,[23] is that Coulomb repulsion between the positively charged antisites (which occur in greater numbers in Be-doped LT GaAs) , or between charged antisites and positively charged precipitates, slows down the formation of the As precipitates during annealing. (A reduction in gallium vacancy concentrations, leading to suppression of the vacancy-assisted diffusion of As antisites, was ruled out by positron annihilation studies, which showed that the Ga vacancy concentration was the same in undoped and Be-doped LT GaAs.[23])

In our work on arsenic interstitial diffusion, it appears that the most rapid mechanism for diffusion involves transitions between the neutral or -1 charge state and the $+1$ charge state, since the neutral or negatively charged arsenic interstitial prefers to share an arsenic site, and the positively charged arsenic interstitial prefers to share a gallium site with the gallium atom that is already there. We find that the potential energy surfaces for these different charge states will allow the interstitial to diffuse along an open-ended, continuous path without going over a large barrier, simply by periodically changing charge. The diffusion rate for an arsenic interstitial in n-type or insulating GaAs therefore depends on the difficulty of switching to a $+1$ charge state; *i. e.* it depends on the Fermi level. However, we would expect arsenic interstitials in LT GaAs to move rapidly enough that they probably do not survive as isolated interstitials for very long – in contrast to arsenic antisites, which have a high enough diffusion barrier that large, non-equilibrium concentrations of antisites can survive in LT GaAs.

Since a major part of the work summarized in this section was carried out by students supported on the affiliated AFOSR grant F49620-97-1-0479, "Augmented Student Participation in Theoretical Investigation of Point Defects and Defect Complexes in Low-Temperature-Grown GaAs", this work will be described in greater detail in the final report for this grant, which concludes in June, 2001.

3. Kinetics of GaAs growth and the influence of growth conditions on
the incorporation of excess arsenic

Since equilibrium energetics alone is not sufficient to explain many features of epitaxial growth (*e. g.* how large, non-equilibrium concentrations of excess As can get incorporated into LT GaAs), understanding the fundamental kinetic processes of growth is an important step toward optimizing the characteristics of the resulting semiconductor layers by altering the growth conditions. For a better understanding of these phenomena, we need to obtain insight into the process of growth on a microscopic scale.

In the past, growth simulations for the III-V compounds have mainly been based on semi-empirical models. These are mostly variants of the solid-on-solid model, with a bond-strength bond-order description of the covalent bonds between atoms. In the simplest case, only one component (Ga) is treated, and diffusion is modeled on a simple cubic lattice.[26-27] More recently, the model has been extended to include the physical cation (fcc) lattice,[28] some kinetic aspects of the arsenic adsorption,[29] or a Schwoebel-Ehrlich barrier.[30] The parameters of these models (*e. g.* bond strengths) are generally "tuned" to reproduce experimental results, such as the oscillations observed in RHEED. Even more recently, more sophisticated growth models have been developed, using information obtained from STM pictures as additional input.[31] In the more refined models, a growing number of parameters must be fixed by fitting to additional sources of information. However, even in these models, several microscopic processes are still lumped together into effective parameters, such as an effective barrier for diffusion (which may involve several steps, adatom hopping by different mechanisms, and in different environments). Here, we often face difficulty in assigning the effective parameters of these models to specific microscopic processes.

In collaboration with Peter Kratzer, Matthias Scheffler, and others at the Fritz-Haber-Institut der Max-Planck-Gesellschaft, we have begun an ambitious program aimed at understanding growth by starting from the microscopic processes: we are using density functional theory to determine the geometry and total energy of numerous microscopic configurations with the help of large-scale electronic structure calculations.[32] In this way, the

relevant processes and parameters of a growth model can be determined from first principles. The results of the calculations can be checked against the information extracted from STM images of growing surfaces. In our work to date, we have considered only MBE growth of GaAs from the elements. The process of MOCVD growth is clearly more complicated. Therefore, first-principles theoretical modeling of this process has not been attempted yet.

3.1 Interaction of arsenic molecules with the ideal GaAs surface

Because of its technological importance as the most commonly used surface for epitaxial growth of GaAs, the GaAs (001) surface has been extensively studied. The relative energies of various static reconstructions for this surface, with different surface stoichiometries, have been investigated by first-principles calculations.[33,34] However, the atomistic processes of growth for this surface are complex and not yet fully understood.

Although both As_2 and As_4 sources are used for epitaxial growth of GaAs, it is simpler to understand the growth processes when As_2 is used, since the GaAs (001) surface reconstructions produced in standard epitaxial growth are terminated with arsenic dimers, so the As_2 molecule does not necessarily have to break up in order to become incorporated into the growing surface. For this reason, we used first-principles, density-functional pseudopotential calculations[6] to investigate the interactions of As_2 molecules with the $\beta2(2\times4)$ and $c(4\times4)$ reconstructions of the GaAs (001) surface.[35,36] Our calculations were carried out using both the generalized gradient approximation (GGA),[4] which gives more reliable binding energies and adsorption barriers, and the local density approximation (LDA), for comparison to earlier calculations.

We have found that an As_2 molecule coming down on the surface initially comes into a region above the surface corresponding to an intermediate plateau in the total energy, as shown in Figure 1. In this region, the addimer behaves as if it is physisorbed: it keeps the bond length of the isolated molecule (2.1 Angstroms), rather than expanding to the bond length of the surface dimers (2.5 Angstroms), and there is very little distortion of the GaAs surface below. While it remains in this region, the arsenic addimer has a binding energy to the surface of about 0.2 eV. As long as the physisorbed addimer is located over the mountains of the $\beta2(2\times4)$ surface, it floats about 2.5 Angstroms above the surface. However, its vertical position over the trenches is not so

well defined, since it can float down into the trench without encountering an energy barrier. Since physisorbed As_2 molecules can move around on the surface without significantly changing their energy or causing large relaxations of the surface atoms below, they should be quite mobile, making it easier for them to find favorable binding sites on the surface and orient themselves so they can bind strongly to these sites before they desorb back into the vapor phase.[35]
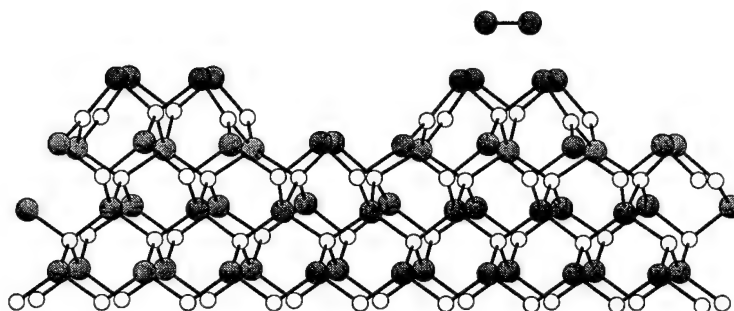

Fig. 1. The $\beta 2(2\times 4)$ reconstruction of the GaAs (001) surface with an incoming arsenic addimer at the preferred "physisorbed" distance above the surface. Arsenic atoms are grey, and gallium atoms are white.

If no gallium atoms are present on the $\beta 2(2\times 4)$ surface, we found that the strongest binding of the arsenic addimer occurs when it comes down on top of the mountain, breaking the bonds of two adjacent arsenic surface dimers and inserting itself into these bonds, as shown in Figure 2. The binding energy of the addimer chemisorbed on the arsenic surface dimers of the mountain is about 1.6 eV.[35]

Experimental work starting with the earliest studies[37-39] shows that arsenic can bind to the surface more effectively when gallium adatoms are present. Earlier theoretical work[40] has shown that the most energetically favorable place for gallium adatoms on the $\beta 2(2\times 4)$ surface is in the trenches. We found that when two gallium atoms occupy adjacent sites in the trench, forming the $\alpha(2\times 4)$ reconstruction, they form a stable nucleus for a growing gallium cluster, which fills

the gallium layer at the bottom of the trench.[32] In local regions where gallium clusters have filled the gallium layer at the bottom of the trenches, additional gallium atoms falling on the surface are forced to stay on the mountains. We found that nearest-neighbor pairs of gallium adatoms on the mountains also form strongly bound, stable dimers.[36]
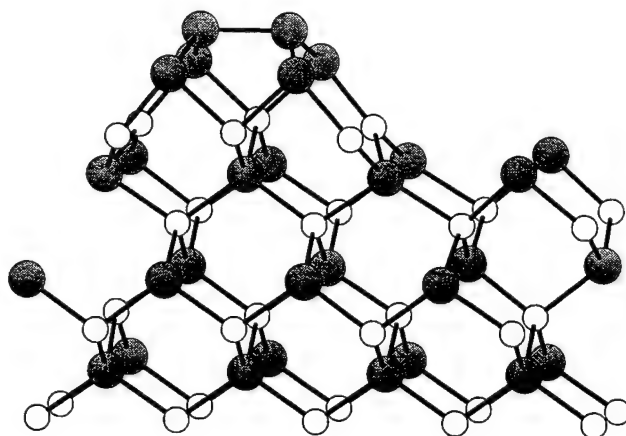

Fig. 2. Arsenic addimer chemisorbed on the top arsenic layer of
the β2(2x4) surface. Arsenic atoms are grey, and gallium atoms
are white.

As$_2$ adsorption on sites with a square array of four dangling Ga bonds is strongly exothermic: we found binding energies of about 2.7 eV for arsenic addimers on top of a cluster of four Ga atoms on the mountain, and 2.4 eV for arsenic addimers on top of a pair of Ga atoms filling the Ga layer in the trench.[36] An arsenic addimer can also adsorb on top of a single Ga atom in the trench, where it has a binding energy of about 1.8 eV. The arsenic atom which has no gallium atom beneath it will tip slightly downward toward the empty gallium site, but the dimer will not dissociate. As in all the other strongly bound adsorption sites we have investigated, the arsenic addimer prefers to remain a dimer. When we separated the arsenic atoms, placing one on top of the gallium atom and the other in the empty gallium site beside, they relaxed back to the tilted dimer configuration.[35]

Once an As_2 molecule has adsorbed on top of a pair of gallium atoms in the trench, locally forming the $\beta(2x4)$ reconstruction in one unit cell, only one more As_2 molecule would have to adsorb beside the first one in the trench in order to completely fill the trench, producing a flat surface. However, we found that further As_2 adsorption on the local β reconstruction is energetically unfavorable.[36] Therefore, we expect that complete filling of the trench does not occur until nucleation of the new mountains of the next layer up changes the structure so that it is no longer locally the β structure.

We note that it may not be easy to distinguish experimentally between a three-dimer $\beta(2x4)$ reconstruction and a four-dimer completely filled trench. In STM images of the $\beta2(2x4)$ surface, the filled dangling bond orbitals of the As dimers in the top layer extend out far enough that the bright stripes corresponding to the two As dimers of the mountain appear considerably wider than the dark stripes corresponding to the two missing dimers of the trench. It seems quite plausible that the three-dimer structure would appear as if it had a completely filled trench in STM pictures, since the filled dangling bond orbitals of the three As dimers in the top layer could extend far enough out to mask the fourth empty dimer site.

Figure 3 shows the growth sequence we have suggested, based on our calculations.[36] Since the gallium atoms which fall on any local area are likely to migrate to the trench sites until the nearby Ga sites in the trench are filled up, we expect that growth will generally proceed by a partial filling of the trenches and formation of the local $\beta(2x4)$ structure, followed by nucleation of the mountains of the next layer up in regions adjacent to locally filled trenches. Since nucleation of the new mountain is expected to proceed before the fourth As dimer adsorbs, completely filling the trench, we see that the new mountain must nucleate above the center or above the sloping sides of the mountains of the original layer, not above the center of the original trench. This may explain why the new mountains are observed[31] to grow above the old mountains in STM pictures, instead of above the trenches.

When the temperature is lowered to 700 K or below, desorption rates are strongly reduced for arsenic addimers at all adsorption sites. If the arsenic overpressure or the incoming arsenic flux is high, the rate of arsenic adsorption on the top arsenic surface layer can exceed the rate of desorption from these sites. This suggests that under arsenic-rich, low-temperature conditions
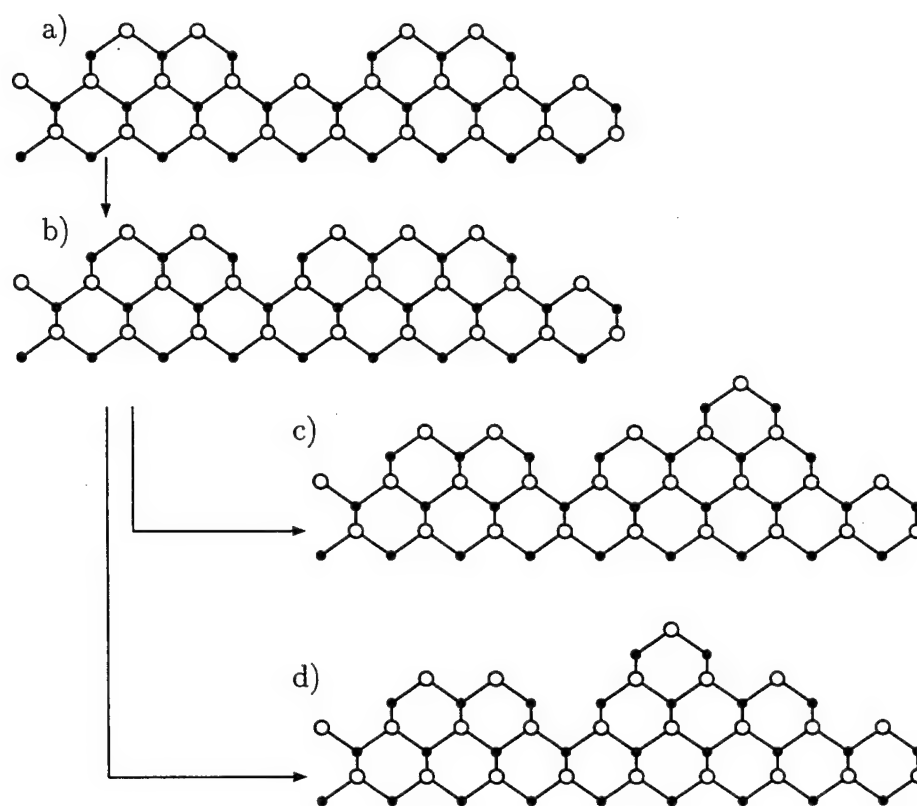
Fig. 3. Growth scenario proposed as a summary of the calculated energetics for growth at the β2(2x4) surface: the local β reconstruction (b) acts as a precursor for nucleation of the new layer (c) or (d). In this schematic picture, arsenic atoms are white and gallium atoms are black.

the surface should transform to a new reconstruction involving a top partial layer of arsenic chemisorbed on arsenic: the c(4x4) structure.

The c(4x4) reconstruction, which is shown in Figure 4 with a single additional arsenic molecule chemisorbed on it, is terminated by a complete layer of arsenic, with an additional partial layer of arsenic on top. Based on our calculations, we can roughly reproduce the experimentally observed boundaries for the transition to the c(4x4) structure.[35]

When an As_2 molecule comes down on the c(4x4) surface, we found that the molecule will initially come into a region where it acts as if it is physisorbed, just as incoming As_2
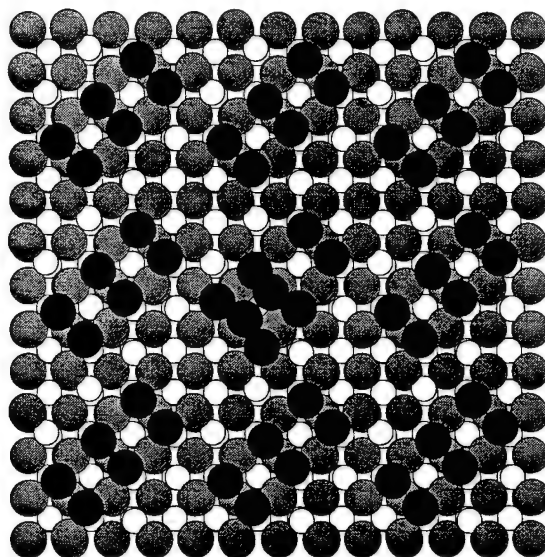
Fig. 4. One arsenic addimer chemisorbed on the surface dimers
of the top partial layer of arsenic for the c(4x4) surface, viewed
from above. The arsenic atoms of the top partial layer and the
addimer are black, arsenic atoms in the lower layers are grey, and
gallium atoms are white. For ease of viewing, the atomic radii are
taken to be larger in this figure than in the other figures.

molecules do on the β2(2x4) surface. If no gallium atoms are present on the c(4x4) surface, the
arsenic addimer can bind strongly on top of two adjacent dimers in the top partial layer, by
breaking these dimer bonds and inserting itself.[35] The bonding configuration for the addimer
chemisorbed on these arsenic dimers looks very similar to the bonding configuration for the
addimer chemisorbed on the arsenic dimers of the β2(2x4) surface, shown in Figure 2.

Under sufficiently low-temperature, arsenic-rich conditions, we expect that arsenic
addimers will chemisorb randomly at one end or the other of each group of three surface dimers
in the top partial layer of arsenic, causing the c(4x4) RHEED pattern to become fuzzier. If this is
followed by further random arsenic adsorption at more weakly bound sites, the c(4x4) ordering

may disappear completely. Such a change from the c(4x4) pattern to a disordered (1x1) pattern has been seen experimentally[41-42] at low temperatures and extremely high arsenic fluxes.

The enhanced chemisorption of As_2 molecules on the arsenic surface dimers which occurs under low-temperature, arsenic-rich conditions can also explain the well-documented observation that MBE growth of GaAs under such conditions leads to incorporation of up to (1-2)% excess arsenic, which can produce technologically attractive, high-resistivity material with ultrashort carrier lifetimes.[43]

3.2 Kink formation and interaction of kinks with excess arsenic

As the substrate temperature is lowered, an additional distinct "surface phase", which has been called the "γ(2x4) phase", appears in between the β2(2x4) and the c(4x4) phases.[44] The "γ phase" is characterized by a large concentration of kinks in the mountain rows on the surface, to the extent that the mountain rows of the γ surface appear to be full of curves in STM pictures. This is quite different from the behavior seen in STM pictures for the mountain rows of the β2 surface, which are extremely straight, extending for long distances without a single kink. Temperature programmed desorption experiments[45] have suggested that the "γ(2x4)" surface contains a variable amount of excess arsenic, and that the "γ(2x4)" surface contains more excess arsenic than the β2(2x4) surface and less than the c(4x4) surface.

Tight-binding calculations[46-47] have indicated that if it is possible to raise the arsenic chemical potential enough to force a small additional amount of excess arsenic (0.03-0.25 monolayers) to adsorb on the β2(2x4) surface, then it would be energetically favorable for the surface to reconstruct so that the excess arsenic could be accommodated as single arsenic atoms in the trenches, each sitting beside a kink. In other words, if it is possible to raise the arsenic chemical potential enough, the formation energy for arsenic-decorated kinks could go to zero, resulting in a phase transition to a new surface structure, characterized by a high concentration of kinks in the trench and mountain rows. This would also lead to a variable concentration of excess arsenic, but a higher concentration of excess arsenic than would be observed for the ideal β2(2x4) surface. The suggested structure of these arsenic-decorated kinks is shown in Figure 5.

However, there is a limit to how high the arsenic chemical potential can be raised. The

most arsenic-rich environment for a GaAs surface in equilibrium is when it is in equilibrium with pure bulk arsenic. This earlier work[46-47] did not include a calculation of the formation energy of arsenic-decorated kinks to verify that the formation energy goes to zero in the arsenic-rich limit (corresponding to a surface in equilibrium with bulk arsenic) – and indeed it is not possible to calculate such formation energies reliably using tight-binding methods.

We have used first-principles density-functional methods to calculate the formation energies of bare kinks, and kinks decorated with several different low-energy, arsenic-rich structures in the neighboring trench, in the arsenic-rich limit. The bare kink does not have an extra arsenic atom inserted into the last arsenic dimer in the trench beside the kink as shown in
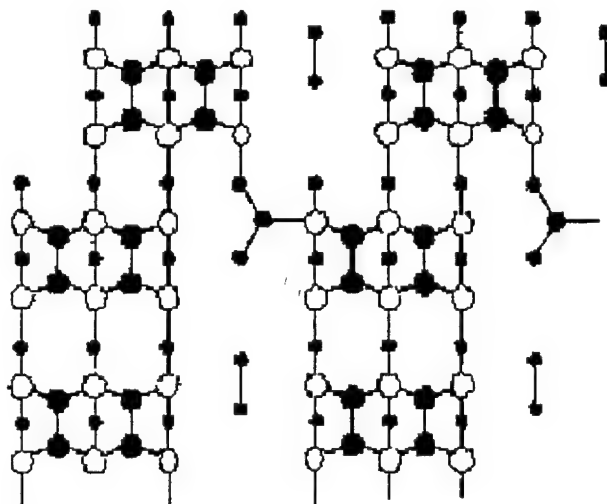

Fig. 5. Top view of a line of kinks in the mountain rows of the β2(2x4) surface, with one arsenic adatom inserted in the last arsenic dimer in the trench beside each kink. Arsenic atoms are black and gallium atoms are white, and atoms near the top of the mountains (which are closer to the viewer) are drawn larger. It has been suggested by Goringe et al.[46-47] that the formation energy of this arsenic-decorated kink configuration goes to zero as conditions become more arsenic-rich, producing a transition to the "γ(2x4) phase".

Figure 5. One of the atoms forming this dimer cannot move as far toward its partner as it does in the absence of the kink, because the neighboring mountain is now sitting on top of it. However, we found that this last trench dimer forms anyway, rather than leaving an unbonded arsenic atom beside the kink.

We found that the formation energy for a line of bare kinks is about 0.8 eV per mountain which is shifted if neighboring lines of kinks are separated by a distance equivalent to two arsenic dimers along the trench, and about 0.7 eV per mountain if we double the distance between the neighboring lines of kinks. We found that the formation energy of a line of arsenic-decorated kinks, as shown in Figure 5, is also about 0.8 eV per mountain if the kinks are separated by a distance equivalent to two arsenic dimers along the trench, and about 0.7 eV per mountain if we double the distance between the neighboring lines of kinks. The arsenic-decorated kink structure shown in Figure 5 is the lowest energy kink structure involving excess arsenic which we have found. A kink with an extra gallium atom bridging the arsenic dimer in the trench beside the kink, with an additional arsenic dimer on top of it, has a formation energy of about 1.1 eV per mountain if the neighboring lines of kinks are separated by a distance equivalent to two arsenic dimers along the trench.

Although the calculated formation energy for a line of kinks separated by four arsenic dimers along the trench (about 33 Angstroms) from neighboring lines of kinks may not have completely converged to the formation energy for an isolated line of kinks, formation energies for the most energetically favorable arsenic-decorated kinks as well as for bare kinks should be reasonably close to our calculated values of 0.7 eV per mountain. These results indicate that the energy cost to form a line of kinks extending through the crystal, producing kinks in a large number of adjacent mountain rows, is prohibitively high.

STM pictures taken shortly after a growth interruption show many small islands for MBE growth on the GaAs (001) surface, while growth on the (110) and (111) surfaces produces fewer and larger islands at the same nominal coverage.[48] This is in agreement with our first-principles calculations, discussed in Section 3.1 above, which indicate that a pair of gallium atoms in the trench already forms a stable nucleus for growth of an island on the (001) surface. As growth proceeds, and the mountains of the new layer nucleate in regions where the gallium layer in the

trench has been locally filled in, the crystal structure dictates that these mountains must be shifted slightly to one side or the other relative to the mountains in the layer below (see Figure 3 in Section 3.1). Since the position in which the mountains of the new layer are created depends on the random growth processes involved in the nucleation of each island, kinks in the mountain rows may often result from the growing together of two adjacent islands.

However, our results for kink formation energies indicate that both arsenic-decorated and bare kinks cost too much energy to be present in appreciable numbers in equilibrium. So it is not surprising that almost all of the kinks manage to anneal out if the temperature is high enough during the short time between the growth interruption and the STM scan, producing the extremely straight mountain and trench rows which are normally seen for the $\beta2(2x4)$ surface. At lower temperatures, the substrate cannot reach equilibrium – the large, non-equilibrium concentrations of kinks resulting from the coalescence of many small islands cannot anneal out, so many kinks remain after growth. We conclude that the "γ phase" is in fact not a stable equilibrium phase, but a manifestation of the fact that at lower growth and annealing temperatures, the kinks are kinetically unable to anneal out.

In qualitative agreement with the earlier tight-binding calculations, we found that it costs no energy for excess arsenic atoms to adsorb in the trench adjacent to a kink site, in the arsenic-rich limit (*i. e.* for a surface in equilibrium with bulk arsenic). In contrast, we found that it costs about 0.7 eV for a single arsenic atom to adsorb in the trench on the ideal, kinkless $\beta2(2x4)$ surface in the arsenic-rich limit. Therefore, we do not expect appreciable numbers of single arsenic adatoms to be present on the ideal $\beta2$ surface. We believe that the additional amount of excess arsenic which is observed to be present in the "$\gamma(2x4)$" surface results from the adsorption of arsenic at the many kink sites which remain on the surface when the substrate temperature is too low to allow the kinks to anneal out. Some of the excess arsenic atoms in the trenches beside arsenic-decorated kink sites may become buried as growth proceeds, rather than being displaced by diffusing Ga adatoms, so these arsenic adatoms may act as precursors for As antisites.

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4. Publications/Presentations/Degrees Granted

Publications

"Arsenic Interstitials and Interstitial Complexes in Low-Temperature-Grown GaAs," J.I. Landman, C.G. Morgan, J.T. Schick, P. Papoulias, and A. Kumar, Physical Review B **55**, 15581-15586 (1997).

"Arsenic Interstitial Pairs in GaAs", P. Papoulias, C. G. Morgan, J. T. Schick, J. I. Landman, and N. Rahhal, Materials Science Forum **258-263**, 923-928 (1997).

"Density-Functional Theory Studies on Microscopic Processes of GaAs Growth", P. Kratzer, C. G. Morgan, and M. Scheffler, Progress in Surface Science **59**, 135-147 (1998).

"Arsenic Dimer Dynamics during GaAs Growth: Theoretical evidence for a novel chemisorption state of As2 molecules on GaAs surfaces", C. G. Morgan, P. Kratzer, and M. Scheffler, Physical Review Letters **82**, 4886-4889 (1999).

"Model for Nucleation in GaAs Homoepitaxy derived from First Principles", P. Kratzer, C. G. Morgan, and M. Scheffler, Phys. Rev. B **59**, 15246-15252 (1999).

"First-principles Study of a Nearest-neighbor As Interstitial Pair in GaAs", J. T. Schick, C. G. Morgan, and P. Papoulias, submitted to Physical Review B.

"Thermodynamic Stability of Kinks on the GaAs (001) Surface", C. G. Morgan, P. Kratzer, and M. Scheffler, in preparation.

Presentations

"As Interstitials and As Antisites in Low-Temperature -Grown (LT) GaAs", C. G. Morgan, Institute of Semiconductors, Chinese Academy of Sciences, Beijing, China, May 27, 1996.

"Arsenic Interstitials and Interstitial Complexes in Low-Temperature Grown (LT) GaAs", C. G. Morgan, J. T. Schick, J. I. Landman, P. Papoulias, A. Kumar, and A. M. Tischler, Gordon Conference on Point and Line Defects in Semiconductors, Andover, NH, Aug. 21, 1996.

"Interstitials and Defect Complexes in Low-Temperature Grown (LT) GaAs", C. G. Morgan, J. I. Landman, P. Papoulias, and J. T. Schick, Psi-k Workshop on First - Principles Molecular Dynamics, Fritz - Haber-Institut, Berlin, `Germany, Nov. 5, 1996.

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"Theory of Defect Structures in LT GaAs", C. G. Morgan, P. Papoulias, J. I. Landman, J. T. Schick, A. Tischler, and N. Rahhal, AFOSR Contract Review, UC Santa Barbara, Aug. 19, 1997.

"How Can First-Principles Calculations Contribute to a Microscopic Understanding of GaAs Growth?", P. Kratzer, A. Kley, C. G. Morgan and M. Scheffler, International Winter School on the Physics of Semiconductors, St. Petersburg, Russia, Feb. 28, 1998.

"The Role of As_2 in MBE Growth of GaAs", C. G. Morgan, P. Kratzer, and M. Scheffler, March Meeting of the American Physical Society, 1998. Abstract: Bull. Am. Phys. Soc. 43 (1) 916.

"The Role of Arsenic Adsorption in MBE Growth of GaAs", C. G. Morgan, P. Kratzer, and M. Scheffler, Forschungszentrum Juelich, Germany, April 11, 1998.

"The Role of Arsenic Adsorption in MBE Growth of GaAs", C. G. Morgan, P. Kratzer, and M. Scheffler, International Workshop on Nanostructures at Surfaces and Interfaces, Monte Verita, Switzerland, April 20, 1998.

"MBE Growth of GaAs: The Role of the As_2 Dimer", C. G. Morgan, P. Kratzer, and M. Scheffler, Tenth Conference on Semiconducting and Insulating Materials, Berkeley, CA, June 1, 1998.

"A Model for Nucleation in GaAs Homoepitaxy Derived from First Principles", P. Kratzer, C. G. Morgan, and M. Scheffler, Ninth International Workshop on Computational Materials Science, Trieste, Italy, Jan. 1999.

"Nucleation in GaAs Epitaxial Growth", P. Kratzer, C. G. Morgan, and M. Scheffler, March Meeting of the American Physical Society, 1999. Abstract: Bull. Am. Phys. Soc. 44 (1, Part II) 1460.

"Investigations of Nucleation in GaAs Homoepitaxy", P. Kratzer, C. G. Morgan, and M. Scheffler", March Meeting of the German Physical Society, Regensburg, Germany, March 1999.

Invited Talk: "First-Principles Study of Elementary Processes of GaAs Growth", P. Kratzer, C. G. Morgan, and M. Scheffler, 18th European Conference on Surface Science, Vienna, Austria, Sept. 23, 1999.

"First-Principles Studies of Growth Processes and Defects in LT GaAs", C. G. Morgan, P. Papoulias, A. Tischler, and J. T. Schick, AFOSR Contract Review, Kettering OH, Sept. 28, 1999.

Invited Talk: "Modeling of Epitaxial Growth: Recent Results for GaAs", P. Kratzer, C. G. Morgan, and M. Scheffler, Symposium on Non-stoichiometric Compounds, Erlangen, Germany, October 1999.

Degrees earned by students who have worked on this research project

Joseph I. Landman, Ph. D., "A Molecular Dynamics Investigation of Low Temperature Gallium Arsenide", thesis defense: July 18, 1997.

Ana Tischler, M.A., "Diffusion in GaAs and GaAs-based Materials", presentation/defense: April 14, 2000.

Panagiotis Papoulias, Ph.D., "Arsenic Interstitials and Interstitial-Containing Complexes in GaAs", in preparation.

## 6. Appendix A: Arsenic Binding Sites at the GaAs (001) Surface

Some binding sites for the As_2 molecule at the $\beta2(2\times4)$ surface are shown below. Binding energies at these sites are given relative to an As_2 molecule infinitely far from the surface. Sites with binding energies less than 1.5 eV are temporary sites for commonly used growth and annealing conditions. Sites with binding energies greater than 1.5 eV are stable binding sites for commonly used low-temperature, arsenic-rich growth and annealing conditions, and sites with binding energies greater than 2.0 eV are stable for commonly used high-temperature growth conditions.

The final binding configuration shown is the strongest bound configuration for an isolated arsenic atom in the ideal trench (*i. e.* not beside a kink). The binding energy for the single arsenic atom at this site is given relative to half of an As_2 molecule infinitely far from the surface.
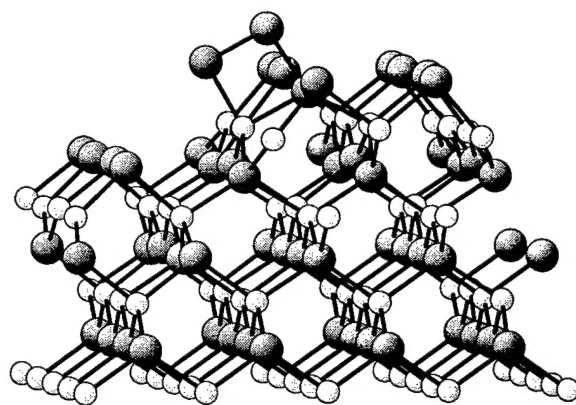
The colors of the atoms are given as follows: As ●   and Ga ○.
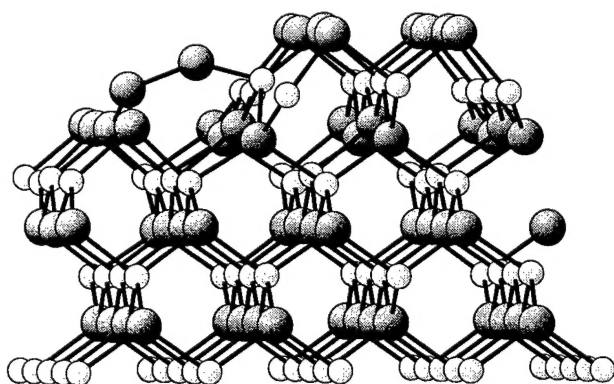
Molecular As_2 adsorption
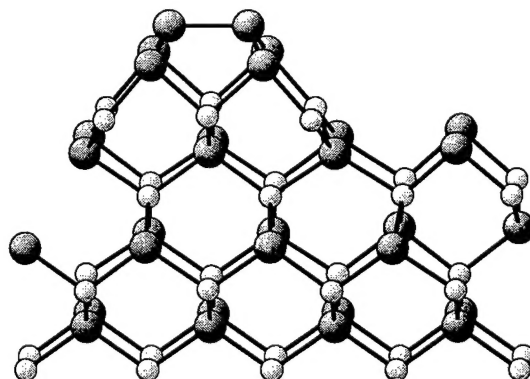Binding energy: ~0.2 eV
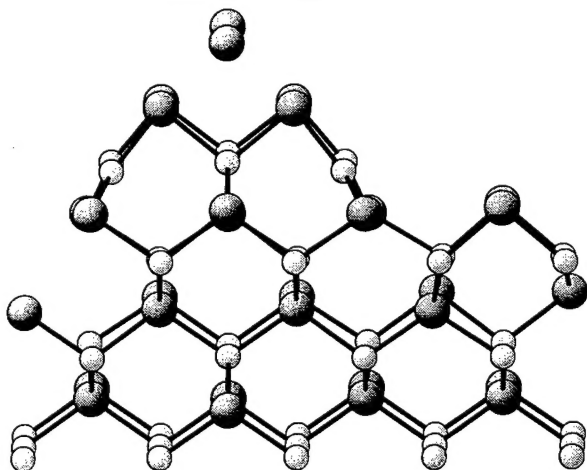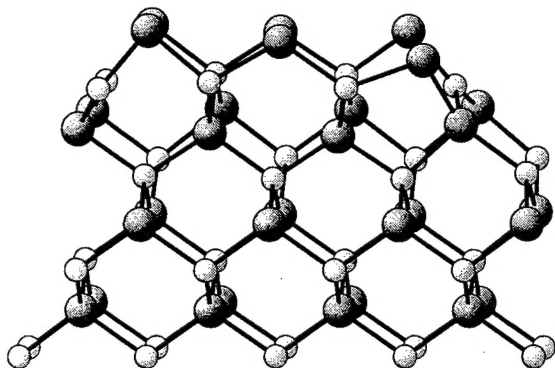
Binding energy: 0.9 eV
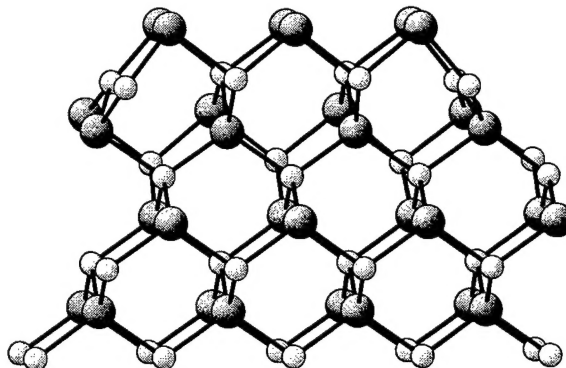
Binding energy: 1.4 eV

Chemisorbed on mountain
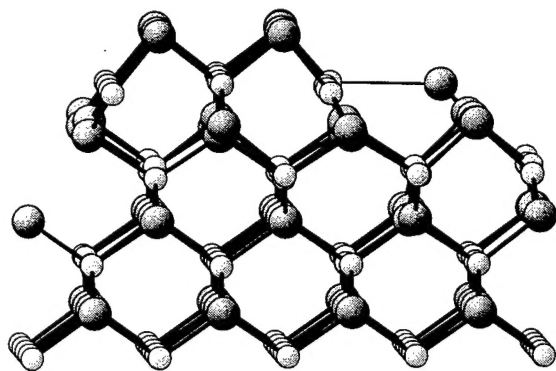Binding energy: 1.6 eV

On one Ga in trench
Binding energy: 1.8 eV

On two Ga in trench
Binding energy: 2.4 eV

Single As in trench
Binding energy: ~0.16 eV

7. Appendix B: Gallium Clusters at the GaAs (001) Surface

The progression from single gallium adatoms to the building of a gallium cluster in the trench of the $\beta2(2\times4)$ surface is shown below, seen from the top. The atoms of the original surface have the same colors as in Appendix A: As ● and Ga ○. So that they can be easily identified, the gallium adatoms are black.

Mobile Ga

-0.6 eV
per
atom

Trapped Ga

-0.6 eV

-0.3 eV

Ga Clusters
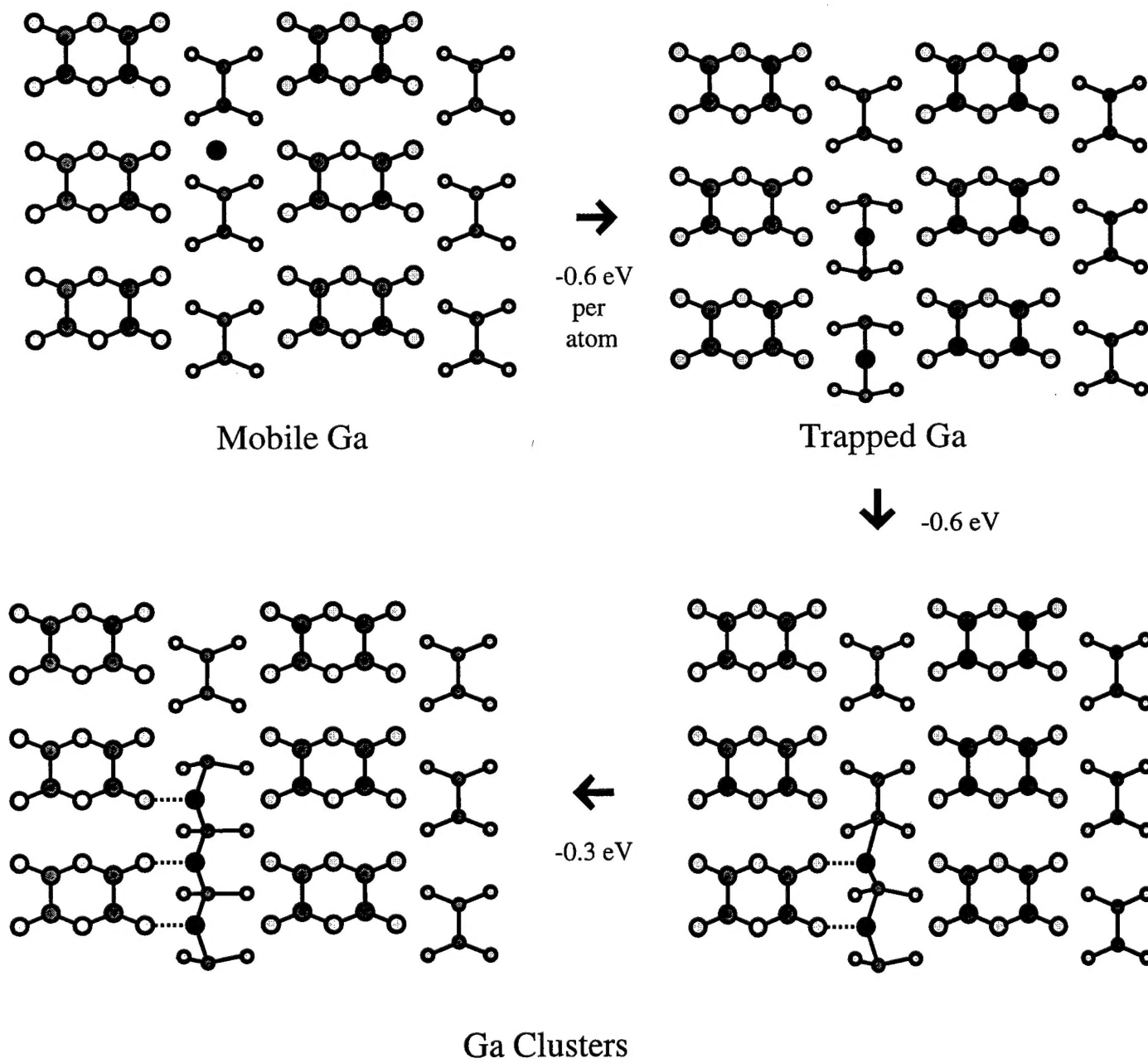
<u>Energies relative to isolated Ga adatoms trapped in the trench,</u>
<u>for trench sites:</u>
Mobile Ga   +0.6 eV
Pair of Ga in trench   -0.6 eV
Cluster of 3 Ga in trench   -0.9 eV
<u>for mountain sites:</u>
Single Ga trapped in mountain dimer   +0.2 eV
Ga dimer chemisorbed on the mountain   -1.0 eV
Pair of adjacent Ga dimers on mountain   -0.2 eV

Hopping rate $\sim 10^5$ /sec at 800K for Ga atoms trapped in trench dimers
$\rightarrow$ thermal distribution of Ga atoms